RADIATION POLYMERIZED GRAFT COPOLYMERS FOR LEATHER

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Radiation cured coatings for leather have been discussed in a series of publications (1-10). Somewhat less attention has been focused on the use of radiation polymerization of vinyl monomers within the leather to modify its properties in spite of an early suggestion by Buechler (1, 3) that this should also be possible and should be considered for full grain (unbuffed) leathers.

The reasons for this suggestion arose from the trend in the shoe upper leather industry to replace lightly buffed leathers split from cattle hides to a desired thickness with unbuffed full grain leather split to a similar thickness. The ratio of the corium minor (grain layer) which contains fine collagen fiber bundles to the deeper corium major layer varies with the thickness to which the leather has been split but is usually less than 1.0. In multiple creasing of the leather, as occurs in the vamp of a shoe, the coarse fiber structure in the corium major frequently dominates the fine fiber structure in the corium minor and leads to unsightly folds. Buechler (11) has shown that the impregnation of the buffed grain layer with preformed polymer improved both the aesthetics and durability of the leather. Scuff resistance of the leather is greatly improved by the impregnation treatment. The polymer impregnant should have a low glass transition temperature, high molecular weight and compatibility with the fibrous component of the leather, the collagen fibers. Polymers employed have included alkaline-solubilized acrylic polymers in water (12), soluble acrylic polymers (13), soluble polyurethanes (14) and co-reacted polyurethane and acrylic polymers (15). Due to greater ease in handling, lower cost and better creasing improvement the acrylics have been favored. The approach described in this paper has been to use a low molecular weight oligomer dissolved in monomers to penetrate into the corium minor of full-grain leathers and then radiation polymerized in situ using either electron beams (EB) or ultraviolet light (UV). When ultraviolet irradiation was employed a photosensitive initiator had to be employed to produce free radicals.

EXPERIMENTAL

The oligomer/monomer solutions were applied to the grain surface of the leather with a thoroughly wet plush swab. The solutions were rapidly absorbed. The swab was then wiped semi-dry and used to wipe off excess from the surface.

Radiation with electron beams was carried out using an Energy Sciences Corp. EB unit. Most impregnation work utilized 200 KEV electrons. Dosages were varied from 0.5 to 6 megarads during the course of the experiments. Polymerization occurred in seconds.

Polymer content was determined by changes in hydroxyproline and extractables after impregnation and polymerization. Bound (unextractable) polymer may not be truly grafted (16) but was reported as such in accord with custom. As will be seen below there is evidence of at least mechanical interaction between polymer and leather.

Depth of polymer penetration was determined histochemically using special adaptation of method using Sandocryl Brilliant Red B-4G and an Auramine O counterstain. The microscope employed was a Nikon Optiphot equipped with an ocular micrometer.

Dynamic mechanical testing was carried out with a Rheovibron II dynamic viscoelastometer (Toyo Baldwin Co. Ltd.) (17). The real and imaginary parts of the complex modulus were determined at three frequencies (3.5, 11, and 110 Hz) at an oscillating relative deformation of 3.8×10^{-4}. This instrument measures the amplitudes of the harmonic force and amplitude signals and determines their phase, δ, with a high precision. These data give the real and imaginary parts E' and E" of the complex modulus: $\hat{E} = E' + iE''$, with $\tan \delta = E''/E'$ where E' is the elastic modulus and E" is the loss modulus.

RESULTS

Cross-sections of impregnated and unimpregnated leather are compared in Figure 1. Figure 1A shows a sample of the impregnated grain layer of cattlehide leather. The dark stain shows the location of radiation polymerized polymer. Figure 1B shows the control area similarly treated histochemically but polymer is absent.

Table I, shows that epoxy oligomer (Celrad 3500) shows less penetration and a lesser amount of bound polymer (lower graft efficiency) than the polyurethane oligomer (Celrad 6700) mixtures. At higher dosage it seemed to benefit more than the others. This may be due to the fact that N-vinyl pyrrolidone (NVP) accelerates cure more than most monomers, and at low dosages some of the somewhat volatile methyl methacrylate may be lost. With NVP present cure is usually fairly complete at absorbed doses in excess of 2.5 Mrad.

Table II, shows the effect of adding 10% (based on the solution) of crosslinker trimethylolpropanetriacrylate (TMPTA). It was expected to increase the amount of unextractable polymer and hence apparent graft efficiency. However, the percent of bonded polymer was already so great that its effect was insignificant except for a little deeper penetration due to decreasing the viscosity of the oligomer solution to which it was added.

Figure 2 shows the dynamic mechanical properties of a film of the mixture described in Table II which had been drawn on a glass plate and cured in an electron beam. There is evidence of two transitions, neither of them sharp, at -35°C and 30°C, respectively. This can be compared with a similar film containing also 2% diethoxyacetophenone as sensitizer, polymerized with ultraviolet light from a Fusion Systems Corporation (Rockville, Md.) conveyorized Model F440 system. The UV light came from a 300 W/in

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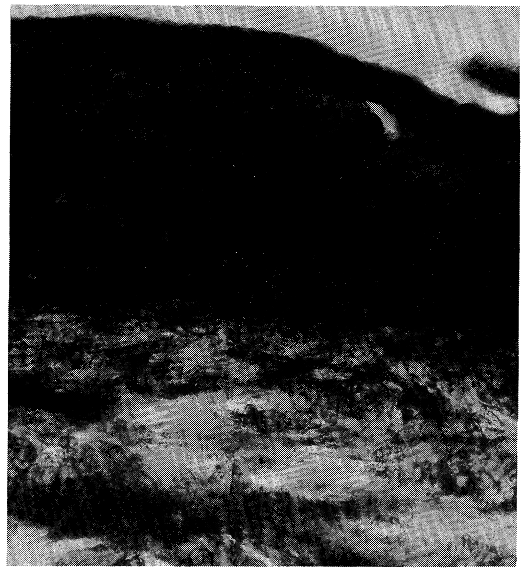
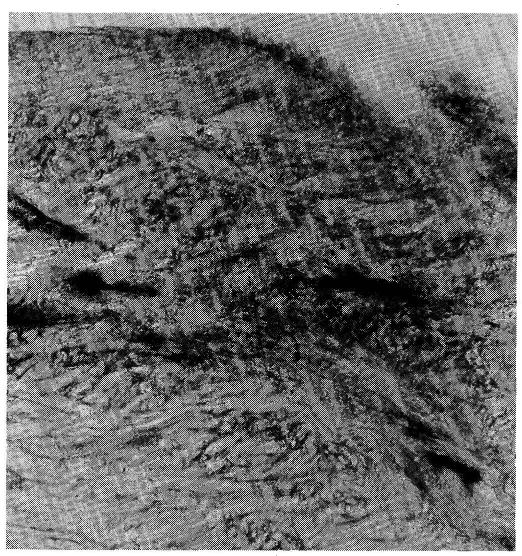
lamp with principal radiation at 210-270 nm; the radiation time was about 1 s. Only one transition is evident in this film, at 25°C, which is very sharp (Fig. 3). Thus the elastic modulus of the electron beam-cured film is orders of magnitude greater than that of the UV-cured film at room temperature but does not abruptly increase between room temperature and 0°C.



1A. Impregnated



1B. Control

Fig. 1. Leather Cross-Sections

TABLE I

Depth of Penetration and Graft Efficiency after EB Cure

Impregnation System	EB Dosage (Mrad)	Depth of Penetration (mm)	Graft Efficiency (%)
50% Epoxy Olig./25% MMA/25% EHA	1.5	0.034	8.61
	3.0	0.050	24.4
	6.0	0.083	63.1
50% Urethane Olig./25% NVP/25% EHA	1.5	0.234	52.5
	3.0	0.246	75.4
	6.0	0.244	87.3
33% Urethane Olig./33% NVP/33% EHA	1.5	0.211	85.0
	3.0	0.176	95.7
	6.0	0.163	75.6

TABLE II

EB CURE (3 Mrad) after Impregnation of Commercial Leathers with 33% Urethane Oligomer/33% NVP/33% EHA

Leather Type	Crosslinking Agent	Depth of Penetration (mm)	Graft Efficiency (%)
Side Leather A	None	0.254	100
	TMPTA	0.432	73.3
Side Leather B	None	0.254	97.9
	TMPTA	0.330	87.9
Pigskin C	None	0.559	71.9
	TMPTA	0.584	76.7

The polymer impregnated layer from an electron beam-cured composite was separated and subjected to dynamic mechanical testing using the Rheovibron instrumentation. The effect of the impregnation on the dynamic mechanical properties of the leather grain layer can be seen by comparing the untreated leather (Figure 4) with the impregnated sample data plotted in Figure 5. The mechanical response of the leather is less sensitive to temperature than that of the composite near room temperature, which shows a vague trace of the underlying glass transition of the polymer. We attempted to model the composite by means of the series-parallel scheme of Takayanagi (18), with his coupling parameter, q, of 0 or 0.3, using the experimentally determined volume fraction of polymer of 0.6. A parameter of q=0 refers to infinite parallel fibers of leather and polymer; that of 0.3, shorter fibers in various directions, which optimizes the fit.

It is clear from the poor fit in both cases that the geometry alone cannot reconcile the very large shift in transition temperature from 30°C in the film down to about 10°C or lower in the impregnated sample. The shapes of the q=0 calculated curves in Fig. 5 resemble those of the sample curves, although shifted to higher temperatures, but the q=0.3 curves represent the data better. In fact, from the dynamic mechanical properties alone one would not discern that the same polymer mixture was used in the film and in the leather grain. It appears that ingredients of the leather have altered the character of the polymer, such as with shorter polymer chains initiated or terminated by radicals formed in the collagen or a lower degree of crosslinking.

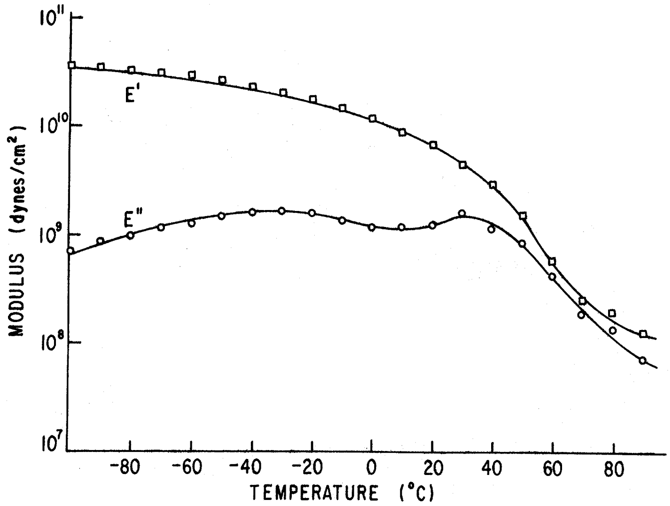


Fig. 2. EB Cured Film (PU/NVP/EHA = 1/1/1)

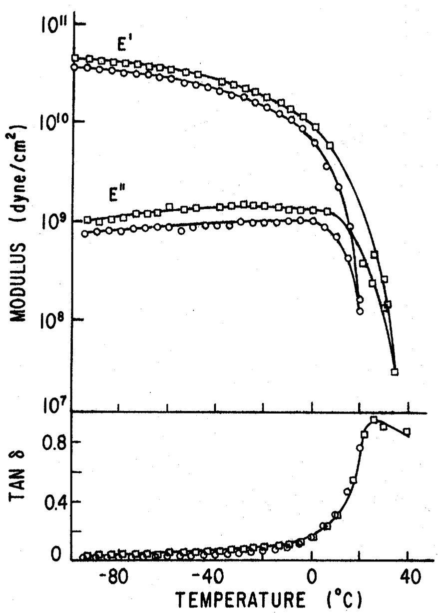


Fig. 3. UV Cured Film (PU/NVP/EHA = 1/1/1)

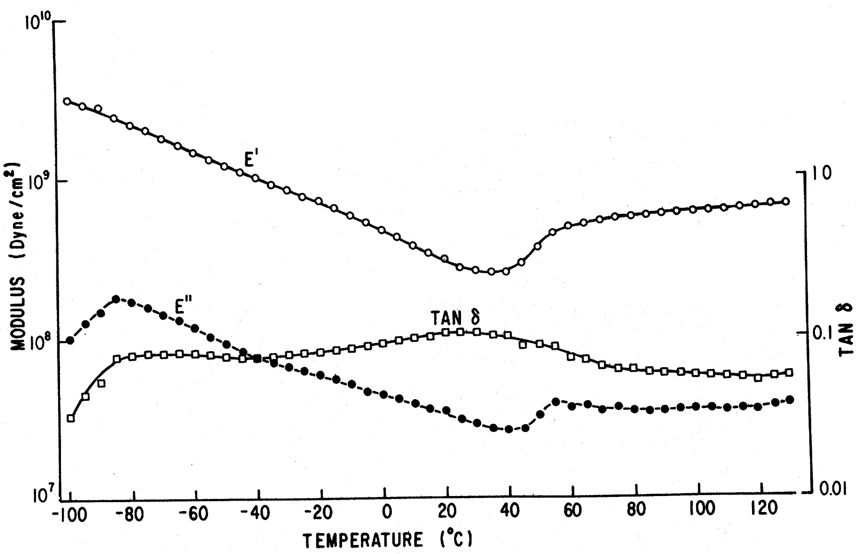


Fig. 4. Untreated Grain Layer

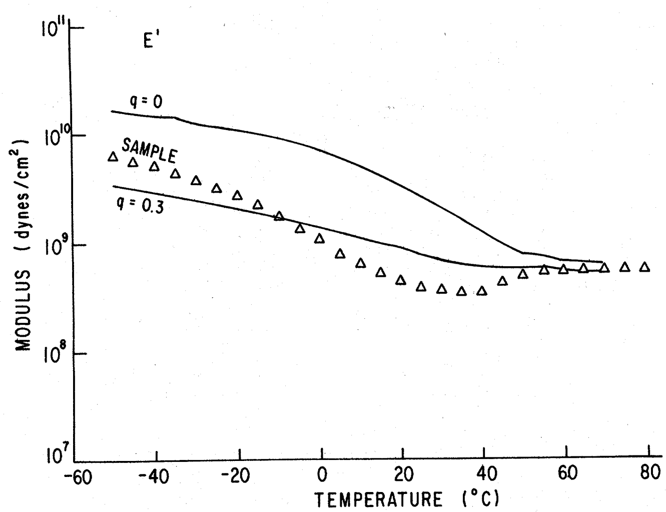


Fig. 5A. Comparison of Takayanagi Models with EB-Cured Composites

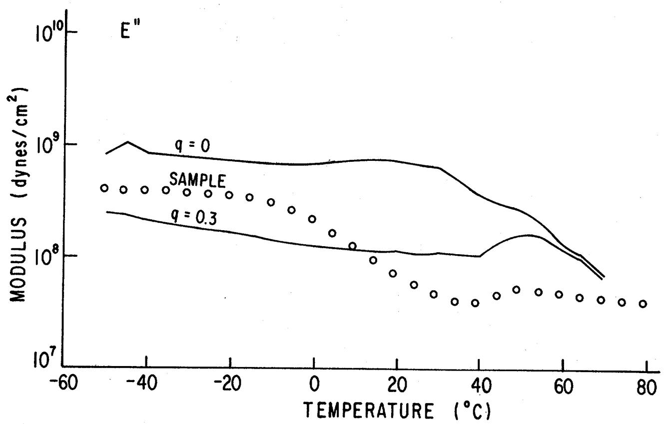


Fig. 5B. Comparison of Takayanagi Models with EB-Cured Composites

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